SYNTHESIS AND CHARACTERIZATION OF A NOVEL BLOCK COPOLYMER CONTAINING DONOR AND ACCEPTOR BLOCKS

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INTRODUCTION

Supra-molecular or nano-structured electro-active polymers find their potential applications in developing variety inexpensive and flexible shaped electronic or opto-electronic devices [1]. In the case of organic photovoltaic materials and devices, for instance, Tang [2] demonstrated that photo generated electrons and holes can be effectively separated and stabilized by the interface of a double layered structure containing organic donors (D) and acceptors (A). Since then, variety donor/acceptor multi-layered, blend or copolymer systems have been studied for potential high efficiency organic photovoltaic devices [3]. Block copolymers are well known for their excellent bicontineous phase separated characteristic [4]. Both morphological pattern and the phase sizes can be easily fine-tuned by the design of each block. We recently presented our preliminary studies of designing and synthesizing controlled-sized donor and acceptor conjugated polymer blocks [5]. In this paper, we present preliminary results of synthesis and characterizations of coupled donor and acceptor block copolymers and some of their electronic and optical properties.

EXPERIMENTAL

All starting materials, reagents and solvents were purchased from commercial sources and used directly except noted otherwise. NMR data were obtained from a Bruker Avance 300 MHz spectrometer. Elemental Analysis was done on a Perkin-Elmer PE4200 Elemental Analyzer, or by Atlantic Microlab Inc. Polymer molecular weight analyses were done using a Viscotek T60A/LR40 triple-detector GPC system with mobile phase of THF at ambient temperature (Universal calibration with polystyrene is used). UV-VIS spectra were collected using a Varian Gary-5 spectrophotometer. Luminescence spectra obtained from an ISA Fluoromax-3 spectrophotometer. For the spectroscopic measurement of polymer solutions, methylene chloride was used as the standard solvent. FT-IR data were obtained from a Bruker IFS-66 IR spectrometer. Polymer films were prepared from spin coating or drop-drying the polymer solutions (0.2 micron filtered methylene chloride) on pretreated glass slides, and the films were typically dried overnight in heated vacuum oven before any analysis. Thermal analyses were done on a Perkin-Elmer TGA6/DSC6/TMA7 system. electrochemical data were obtained from a Bioanalytical (BAS) Epsilon system. In CV measurements, the concentration of polymer solutions (in methylene chloride) was typically 2mM, and the salt (Bu)₄NPF₆ concentration was 0.1M. Reference electrode was a standard Silver electrode. The CV scan rate was 100mV/s.

A general synthetic scheme (Figure 1) is as follows: In scheme (a), one molar quantity acceptor block [6] was added slowly and drop wisely into access amount (more then 2 molar quantity) of bridge blocks [5] in a polar aprotic solvent (such as dichloromethane) under reflux to yield B-A-B (Scheme (b) shows similar reaction for donor block) [7]. In the next step, B-A-B was reacted with about equal amount of donor (D) block yielding final (B-A-B-D)_n block copolymers and time, or by the initial monomer ratios, and that the reaction were quenched by adding an extra amount of one monomer or adding a terminating molecule [7].

$$(\text{EtO})_2 \underset{\text{O}}{\overset{\text{RO}}{\bigcap}} \underset{\text{SO}_2 R}{\overset{\text{O}}{\bigcap}} \underset{\text{SO}_2 R}{\overset{\text{O}}{\bigcap}}$$

Acceptor Block (A)

Donor Block (D)

Bridge Block (B)

a)
$$A + 2B \rightarrow B-A-B \xrightarrow{D} -(B-A-B-D)-$$

b)
$$D + 2B \rightarrow B-D-B \xrightarrow{A} -(B-D-B-A)$$

Figure 1. Synthetic Scheme of the block copolymers

RESULTS AND DISCUSSION

For certain materials functions, the sizes of the donor or acceptor blocks are critical [5]. In our approach, different sized blocks were prepared via either reaction condition (such as reaction length or temperature) or monomer ratio control [7]. The size of the bridge block can be varied using different length linear chain alkane dibromide. While the donor block and acceptor block film has a strong luminescence emission band at about 560 nm and 520 nm respectively, the final -B-D-B-A- block copolymers have a very weak and broad emission band between 520-560 nm, an indication of photo-induced electron transfer and charge separation due to the molecular orbital overlaps between donor blocks and acceptor blocks. Details will be presented and reported [7].

CONCLUSIONS

Preliminary results on the synthesis and characterization of a novel (B-A-B-D)_n type conjugated block copolymer system are presented. The key synthetic strategy includes the synthesis of each individual block first, then couple the blocks together. The size of each block can be adjusted via synthetic conditions or monomer ratio control. The luminescence quenching of final -B-A-B-D- block copolymer indicates electron transfer and charge separation between donor and acceptor blocks. The system is very promising for potential inexpensive and high efficient opto-electronic applications.

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